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(54) Title: RESIN USE FOR TACKIFICATION

(57) Abstract

The invention concerns formulations for hot melt pressure sensitive adhesives. The formulation includes an adhesive formulation for hot melt pressure sensitive adhesives including a styrene-butadiene block copolymer and a petroleum resin produced by copolymerising using a Friedel Craft catalyst, a mixture of (1) from 40 to 90 wt % of a feed comprising C5 olefins and/or diolefins, and/or C6 olefins and/or diolefins; (2) from 10 to 50 wt % of a feed comprising C8-C10 aromatic compounds the wt % being calculated on the basis of the total weight of polymerisable feed components. The resin should possess (a) a level of aromaticity of from 13 to 45 wt % as determined by proton NMR, (b) a softening point of from 50 to 100 °C, (c) an Mn of from 400 to 900 and an Mz of below 2200 and Mw below 1300 and a ratio of Mw/Mn of from 1.2 to 1.7

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RESIN USE FOR TACKIFICATION

Field of invention

The invention relates to adhesive formulations including those with styrene-butadiene block copolymers and petroleum resins used as tackifier in such for formulations.

The adhesive formulation may be used as a pressure sensitive adhesive including hot melt pressure sensitive adhesives (HMPSA) and be of use particularly in applications such as label stock and tapes.

Background of the invention

Currently SIS polymer are used for tapes and not the cheaper SBS polymer because SIS can be tackified by C_5/C_6 (di)olefin derived resin having an MW of 1500-2000. SBS based formulations have not to date been tackified so as to provide acceptable tack loss upon aging as SIS.

Tackifiers for SBS with relatively low molecular weights prepared by using a Friedel-Craft catalyst and polymerising a mixture of C5/C6 (di)olefins and C8/C10 aromatics are disclosed in US-A-4078132 (Lepert) and EP-A-23456 (Evans). The softening points are low in EP-A-23456 (Evans).

In Lepert Example 12 molecular weights and aromaticity are high. However the material does not tackify SBS satisfactorily. Ball tack is 4 to 30 cm and so is too high.

In Evans such high amounts of chain transfer agent (mono-olefins) are used that the softening point is very low. The product will not provide a good adhesive/cohesive

performance in SBS blends. The liquid resin serves to substitute the oil in hot melt adhesive (HMA) but cohesive performance is reduced.

It is the object of the invention to provide an improved adhesive formulation which have good cohesive strength and acceptable loop tack loss upon aging characteristics.

Summary of the invention

The invention firstly provides an adhesive formulation for hot melt pressure sensitive adhesives including a styrene-butadiene block copolymer and a petroleum resin produced by copolymerising using a Friedel Craft catalyst, a mixture of

(1) from 40 to 90 wt% of a feed comprising C5 olefins and/or diolefins, and/or C6 olefins and/or diolefins;

(2) from 10 to 50 wt% of a feed comprising C8-C10 aromatic compounds the wt% being calculated on the basis of the total weight of polymerisable feed components;

and having

(a) a level of aromaticity of from 13 to 45 wt% as determined by proton NMR,

(b) a softening point of from 50 to 100°C,

(c) an Mn of from 400 to 900 and an Mz of below 2200 and Mw below 1300 and a ratio of Mw/Mn of from 1.2 to 1.7

The C_5 and/or C_6 diolefin and/or olefin containing feed used may be obtained from the cracking of petroleum feedstock. Such feedstocks include naphthas, kerosene, gas oil and vacuum gas oil. These feedstocks usually boil in a range of from 20°C to 550°C.

The petroleum feedstock is cracked, preferably in the presence of steam, and the recommended cracking temperature is between 500°C and 870°C. The product which contains unsaturated hydrocarbons usually boiling in the range of 20°C to 240°C, preferably 20°C to 130°C, generally is thereafter subjected to fractionation to remove C_2 to C_4 light ends. If the feedstock contains large amounts of cyclopentadiene it should be subjected to thermal soaking at a temperature between 100°C and 160°C, preferably 110°C to 140°C. The thermal soaking preferably takes 0.5 hour to 6 hours, e.g. 0.5 to 3 hours to reduce the level of cyclopentadiene or dicyclopentadiene to below 2 wt%. Low temperature heat soaking is preferred in order to limit the cyclic diene (cyclopentadiene and methylcyclopentadiene) co-dimerisation with C_5 linear conjugated dienes (isoprene and pentadienes 1,3 cic- and trans-). After fractionation and, if carried out, thermal soaking, the feedstock is preferably subjected to distillation to remove cyclic conjugated diolefins which are gel precursors (cyclopentadiene and methylcyclopentadiene being removed as dimers).

After distillation one obtains an overhead naphtha which usually boils in the range from 15°C to 100°C, e.g. 25°C to 80°C, the best results being achieved with 25-70°C cut. This overhead naphtha comprises mainly C_5 diolefins such as isoprene and 1,3 cis- and transpentadienes (piperylene), C_5 to C_6 mono-olefins and aromatics, for example, benzene. In general the overhead naphthas have the following compositions:

	% By Weight
Total paraffins	1.0 to 41.5
Total diolefins	50.0 to 14.5
Total olefins	33.5 to 13.0
Total aromatics	20.0 to 35.0
Isoprene 16.5 to 6.5	
Pentadiene 1,3	15.5 to 4.5

The exact composition depending on the nature of the petroleum feedstock which is subjected to steam cracking. Cyclopentene contents are generally below 3.0 wt%. These feeds contain materials such as paraffins and aromatics which are not polymerised during the process of the invention and it is emphasized that these materials are not considered to be part of the reaction mixture for the purposes of this invention.

The feed could be significantly isoprene-free provided this compound is previously recovered through any conventional separation process such as distillation, extractive distillation or azeotropic distillation. In this case, the feed may be a narrow fraction pentadiene 1,3 concentrate. A typical such composition contains less than 5 wt%, preferably less than 2 wt% isoprene, from 25 to 80 wt% pentadiene 1,3 (cis- and transisomer). Other C_5 and/or C_6 olefins, and/or diolefins make up the remainder, generally cyclopentene, typically 75 to 10 wt%.

The C_5/C_6 feed comprises 20 to 70 wt% of the total unsaturated materials in the process of the present invention.

The olefinically unsaturated aromatic compounds useful in the present invention may also by used in its pure form or as mixtures of unsaturated aromatics such as those available from the cracking of petroleum materials. Examples of suitable unsaturated aromatics include styrene, -methyl styrene, indene and vinyl toluene and mixtures thereof. Here again, where mixtures are used, reference to the percentage is to the amount of unsaturated polymerisable aromatic material based fed to the reactor. We prefer to use from 10 to 45 wt% of the unsaturated aromatic compound.

Olefinically unsaturated aromatic compound is from hear cut distillate (HCD) obtained by fractionation can also be used. Its typical composition is Table 1 :

Table 1 :

Total vinylaromatics	50 wt%
Dicyclopentadiene (DCPD)	1 wt%
Higher boiling point than naphtalene (not identified)	15 wt%
Dihydro + tetrahydro DCPD	8 wt%
Non polymerizable aromatics	balance

Agents to narrow the molecular weight distribution may be employed in the production of the resins, for example, the branched chain reactive aliphatic olefins of our GB patent 1538057 for example those obtained by steam cracking may be used to achieve narrow distribution. These olefins may make up part, preferably 10-50 wt % especially 20-40 wt%, of the C_5/C_6 feed and the amount of branched olefins used may be varied to obtain resins of any desired softening point within the range 50°C to 100°C. We prefer to use up to 50 wt% based

on the total weight of unsaturated compounds of these olefins. Where branched olefins are used, a broad (e.g. C_5-C_8) fraction of our U.K. patent 1538057 may be used. The preferred branched chain reactive aliphatic olefins are oligomers of propylene and butylenes obtained with phosphoric acid catalyst or from a Fluid Catalytic Cracker.

Other chain transfer agents such as the alkyl halides of our U.K. patent 1537852 may also be used optionally as part of the catalyst system.

Similarly, oxygenated transfer agents may be used such as mono-, di- or tri-substituted phenols, the substitution being a C_1 to C_{30} or preferably C_1 to C_6 straight chain or branched chain hydrocarbyl group, e.g. methyl, ethyl, propyl, butyl, amyl or their secondary or tertiary isomers (e.g. 2,6 ditertiary-butyl-4-methyl phenol), alcohols, esters, dialkyl ethers, alkaryl ethers, the alkyl group in the ether being C_1 to C_6 straight or branched chain hydrocarbyl group, e.g. methyl, ethyl, amyl or their secondary or tertiary isomers, (e.g. anisole), organic acids or anhydrides (e.g. maleic anhydride). When used, the oxygenated transfer agent should preferably have a boiling point lower than 300°C. If low boiling point compounds, e.g. diethyl ether, are used, the polymerisation temperature and pressure should be carefully chosen so as to maintain them in the liquid state.

The most efficient compounds in the presence of $AlCl_3$ are dialkyl ethers or an alkaryl ether, such as anisole, since they act as solvents for the catalysts. Since the polymerisation is usually carried out between 30°C to 80°C, any such additive should be of adequate boiling point in order to maintain it in the liquid phase.

The amount of oxygenated compound used as transfer agent can vary from 0.1 to 5 wt%, preferably 0.5 to2 wt%, based on the weight of petroleum resin feed. They are generally less attractive than the branched chain reactive aliphatic olefins previously described. The feeds are mixed and polymerised using a Friedel Crafts catalyst, for example, aluminium chloride, aluminium bromide or an aluminium chloride/hydrochloric acid/aromatic hydrocarbon complex or aluminium chloride/alkyl halide/aromatic hydrocarbon complex, the aromatic hydrocarbon being preferably alkyl substituted, for example, O-xylene, mesitylene, ethyl benzene, isopropyl benzene and other short or long chain mono-, di- or tri-alkyl benzenes are especially suitable. The alkyl chain can be linear or branched and can vary from 1 to 30 carbon atoms.

Acid liquid $AlCl_3$ sludges obtained as by-products during the alkylation of benzene or any other substituted aromatics (e.g. toluene or xylene) with branched chain olefins can be directly used as catalyst for the above described polymerisation process. The branched chain olefins which are, for example, produced via the boron trifluoride oligomerisation of propylene and fractionation, e.g. C_{12} olefins or C24 olefins, can be alkylated with aromatics producing <u>in situ</u> sludge. As an example, the acidic sludge available from a dodecylbenzene plant provided similar results to the preformed O-xylene $AlCl_3$/HCl liquid complex sludges from other substituted branched or straight chain aromatic production, for example, meta and/or para di-isopropyl benzenes and para-tertiary butyl benzene may also be used.

In the polymerisation process, the amount of catalyst may vary from 0.25 to 3.0 wt%, preferably 0.5 to 1.5 wt% based on the weight of the mixture to be polymerised. The optimum

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concentration depends on the nature of the solvent which affects the solubility of the catalyst as well as on the stirring efficiency inside the polymerisation reactor.

Other Friedel Crafts catalysts like titanium tri- or tetra-chloride, tin tetrachloride, boron trifluoride, boron trifluoride complexes with organic ethers, phenols or acids can also be used but they lead to rather low resin yields and large quantities of liquid oligomers of low value are obtained. Even though these oily oligomers can be upgraded as reactive plasticizer or liquid plasticizer, such catalysts are not recommended. Other possible catalysts can be acidic clays.

Usual polymerisation temperatures are between -20°C and 100°C, preferably between 30°C and 80°C, we find that if lower temperatures are used, the resin colour is improved although there can be a reduction in yield.

After polymerisation, the residual catalyst may be removed by, for example, washing with aqueous solution of alkali, ammonia or sodium carbonate, or by the addition of an alcohol such as methanol and subsequent filtration.

The final resin may be stripped of unreacted hydrocarbons ("raffinate" rich in benzene and/or paraffins/unreactive olefins) and low molecular weight oligomers by stream stripping or vacuum distillation. The finished resin usually has a higher softening point.

The resins prepared as described above contain both aromatic and aliphatic unsaturation and may be hydrogenated to remove color but whilst avoiding reduction in aromatic unsaturation as far as practicable. The hydrogenation may be batch or continuous. Typical examples of catalysts include nickel,

palladium, platinum and molybdenum sulphide Ni-W, Ni-Mo, Co-Mo catalysts with a preferred catalyst being a pre-activated catalyst on a support such as alumina, kieselguhr, activated charcoal, silica, silica alumina and titania.

A hydrogenation process may be used in which a solution of the resin in a suitable hydrocarbon solvent is passed with an excess of hydrogen or hydrogen rich gas over a catalyst.

After hydrotreating, the mixture from the reactor may be flashed and further separated to recover the solvent and hydrogen for recycle and to recover the hydrogenated resin. The solution is flashed and/or distilled in an oxygen-free or minimum oxygen atmosphere to eliminate the solvent, and thereafter, may be steam distilled to eliminate the possible light oily polymers of low molecular weight, known in the trade by name of "fill", preferably with care not to raise the temperature of the resin above 325°C to avoid degrading the colour and other properties of the finished resin.

The polymeric resin can be flaked when the softening point lies above 80 °C as is preferred.

Resins are thus obtained having a Gardner colour in the region of 8 down to a Saybolt colour of 30, a ball-ring softening point of about 50 to 100°C and a high degree of tackiness. These properties enable them to be used for PSA adhesive formulations with SBS, including HMPSA.

The resin so produced can be blended with SBS polymer to give a PSA with good cohesive properties, reduced tack loss upon aging at an economic cost.

Examples

Table 2 shows feed stream compositions used for making five resins, the relevant reaction parameters and resulting resin properties.

The reactor feed was mixed and a paraffinic solvent in the proportions set out in Table 2. The mixture was then polymerised at 60 °C using 1 wt % $AlCl_3$ as catalyst. The conditions used were as follows :

The reaction mixture (as described in Table 2) was fed to a 2 litres glass reactor which was fitted with a mechanical stirrer, a cooler and a catalyst injuction device. 1 wt% of powdered $AlCl_3$ as catalyst based on the total weight of the feed was injected into the reactor which was then held at 50-60°C for 90 minutes. An ammonia solution was added to stop the reaction after the desired reaction time. The resin was then obtained after steam-stripping at 250°C under nitrogen atmosphere.

Table 2 :

	COMPARATIVE		ACCORDING TO INVENTION		
Sample	1	2	3	4	5
Feed compositions					
-Steam cracker derived olefin	23.5	30	30	42	30
-Heart cut distillate	37.5	46	23	24	23
-C_5 diolefin/ olefin with final boiling point of 70 °C (piperylene concentrate)	18	10	24	14.5	-
-light virgin naphtha	21	14	23	19.5	23
Total polymerisable	53	54.5	55	55.5	54.5
Results					
Resin yield	38.5	38	36.5	28	30.5
Fill yield (oligomers)	16	18.5	11.5	14	14
Softening point(°C)	92	88	88	83	82
Gardner colour	7	8	6.5	7-	7-
Aromatic content wt% by NMR *	46.2	53.2	30.8	34.3	32.2
Mn (GPC)	730	620	775	690	785
Mw (GPC)	1100	860	1135	910	1160
Mz (GPC)	2000	1420	1860	1330	2060
Mw/Mn	1.5	1.4	1.5	1.3	1.5
	Note high aromaticity and compare looptack loss upon aging in Table		Combine relatively high softening point, aromaticity in the correct range, low Gardner, low molecular weight		

The steam cracker derived olefin had a typical composition as set out in Table 3.

Table 3:

Typical composition of Steam-Cracker olefins

Total C_5 and C_6 olefins	70 wt%
Total C_5 and C_6 diolefins	1 wt%
Total aromatics	1 wt%
Total saturates (paraffinic)	balance
Typical C_5 olefins :	
2-MeButene-2	19 wt%
Cyclopentene	12 wt%

The HCD portion had a composition as set out previously in Table 1.

The C_5 diolefin/olefin was a piperylene concentrate having a typical composition as set out in Table 4.

Table 4

Isoprene	1.17
Pentene-2 trans.	1.6
Pentene-2 cis.	3.45
2 Me-butene-2	3.59
Pentadiene 1,3 trans.	43.36
CPD	0.59
Pentadiene 1,3 cis.	23.55
1,2 dimethylbutane	0.38
Cyclopentane	14.99
4 methylpentene-1) 3 methylpentene-1)	0.56
3 methylpentadiene 1,4) 4 methylpentadiene-2 cis.) 2,3 dimethylbutene-1)	0.17
Cyclopentane	1.58
4 methylpentene 2	0.06
2 methylpentane	0.22
3 methylpentane	0.03

The light virgin naphtha had the composition set in Table 5.

Table 5 :

Typical Composition of LVN (Light Virgin Naphta) solvent

Total C_5 and C_6 saturates (paraffinic)	$\geq$ 97 wt%
Aromatics	$\leq$ 0.5 wt%
Diolefins, olefins	balance

The softening point was determined by ring and ball (ASTM E-28). The GPC related data in the description and claims on Mn, Mw, Mz and Mw/Mn were calculated after measurements according to the following description. The calibration is set out in Figure 1.

GEL PERMEATION CHROMATOGRAPHY METHOD USED

Resins are run on a GPC 201 Waters instrument equipped with four ultrastyragel columns. These columns are filled with a porous gel having pore sizes ranging from 10^4 down to 100 Angstroms and a resolving power higher than that of microstyragel.

The set of ultrastyragel columns was calibrated with polystyrene standards (Figure 1) to obtain the "universal" calibration. With each sample a reference (sulfur) is injected to take into account the small variations of flow-rate of the pump. Elution time of sulfur is always assumed to be 100 and the calibration is expressed in terms of reduced elution time O = 100 t/ts where t is the elution time of species M and ts is the elution time of sulfur.

For polystyrene following calibration equation was obtained :

$$\mathrm{Ln}\ M = 53.4459-1.79226O+0.0254066O^2-0.133993E-3O^3$$

From this relationship, the "universal" calibration equation is deduced :

$$\mathrm{Ln}\ M\ (n) = -\ 8.8457+1.713\ \mathrm{Ln}\ M$$
$$= 82.7071-3.07014O+0.0435215O^2-229529E-3O^3$$

O = theta

The calibration for the resins described in this patent was established by using 15 reference samples characterized by their number average molecular weight and intrinsic viscosity.

Following calibration equation was thus obtained :

$$Ln\ M = 62.6837- 2.244780+0.03235980^{2}-0.166704E-30^{3}$$

*<u>Determination of the aromaticity of resins</u>

A solution is made up of a known quantity of the resin (approximately 100 mg) and of a known quantity of internal standard in carbontetra-chloride. Of this solution 0.5 ml is taken, deuteroform is added and the quantitative ^{1}H-NMR-spectrum is run.

The integration of the aromatic region (between 8 and 6,4 ppm) is then compared with the integration of the internal standard.

Based on the number of protons involved in the different areas for the aromatic area :

styrene : 5
alpha-methylstyrene : 5
bisubstituted aromatics : 4

The weights of the compounds, and the molecular weights of the monomer-units and the internal standard, the weightpercentage of aromatic functional groups can be determined.

Table 6 shows different formulations of a commercial SBS (Cariflex 1102 Registered Trade Mark) with different resins and the resulting PSA properties. For comparative purposes a SIS (styrene- isoporene-styrene) block copolymer material is also included which is known to have low tack loss upon ageing.

It can be seen that the resins blended with SBS gave adequate looptack ageing so supporting the conclusion that these formulations are an economic replacement of SIS based formulations.

Table 6

	A	B	C	D
Cariflex TR 1102 (SBS)	100	100	100	-
Cariflex TR 1107 (SIS)	-	-	-	100
Resin 1 in Table 6	125	-	-	-
Resin 2	-	125	-	-
Resin 3	-	-	125	-
Escorez 1310	-	-	-	125
Flexon 876	25	25	25	25
Irganox 1076	-	-	-	1
Irganox 1010	1	1	1	-

Coating on mylar; $23 g/m^2$; release STS 3390

PSA PROPERTIES - INITIAL				
180 peel strength (N/cm) PSTC-1	5.7	5.0	5.5	6.0
loop tack (N/25mm) FTM-9	12.7	10.0	15.6	14.5
ball tack (cm) PSTC-6	2	3	2	1.5
shear -RT- (hours) PSTC-7				
- steel 25mm * 25mm	>150	>150	>150	>150
hot shear (min/C)	10/60	30/50	4/70	8/60
saft (C)	70	66	77 cf	85
blend viscosity at 175 °C (Brookfield Viscometer)	37100	36000	39400	56600

OPEN AIR AGING : LOOP TACK (N/25mm) FTM - 9				
Initial	12.7	10.0	15.6	14.5
After 3 days	-	-	15.9	-
After 5 days	9.2	7.6	-	15.8
After 7 days	-	-	18	-
After 9 days	-	-	15.6	-
After 11 days	4.7	9.6	-	16
After 13 days	-	-	14.6	-
After 19 days	9.8	6.2	-	22.5
After 22 days	-	-	15	-
After 27 days	8.7	5.8	-	24 cf
After 28 days	-	-	14.6	-

Thus it has been found surprisingly that the generally accepted inferiority of SBS formulations versus SIS formulation can be overcome to a considerable extent by using a tackifier with very specific characteristics.

CLAIMS

1. An adhesive formulation for hot melt pressure sensitive adhesives including a styrene-butadiene block copolymer and a petroleum resin produced by copolymerising using a Friedel Craft catalyst, a mixture of

(1) from 40 to 90 wt% of a feed comprising C5 olefins and/or diolefins, and/or C6 olefins and/or diolefins;

(2) from 10 to 50 wt% of a feed comprising C8-C10 aromatic compounds the wt % being calculated on the basis of the total weight of polymerisable feed components;

and having

(a) a level of aromaticity of from 13 to 45 wt% as determined by proton NMR,

(b) a softening point of from 50 to 100°C,

(c) an Mn of from 400 to 900 and an Mz of below 2200 and Mw below 1300 and a ratio of Mw/Mn of from 1.2 to 1.7

2. An adhesive formulation according to claim 1 comprising from 100 to 200 parts of resin per 100 parts of styrene-butadiene block copolymer and from 0 to 100 parts of a processing oil per 100 parts of styrene-butadiene block copolymer.

3. An adhesive formulation according to claim 1 or claim 2 wherein the resin is hydrogenated.

4. An adhesive formulation according to any of the preceding claims wherein the formulation includes from 125 to 150 parts of the styrene-butadiene block copolymer resin per 100 parts of and from 25 to 50 parts of a processing oil per 100 parts of the styrene butadiene block copolymer.

5. An adhesive formulation according to any of the preceding claims wherein the resin has a softening point of 80 to 90½C.

6. An adhesive formulation according to any of the preceding claims in which the copolymer is selected from linear, radial, multiarm tapered copolymers having a styrene content of at least 20 wt %, preferably 25 to 45 wt%.

7. A petroleum resin produced by copolymerising using a Friedel Craft catalyst, a mixture of

(1) from 40 to 90 wt% of a feed comprising C5 olefins and/or diolefins, and/or C6 olefins and/or diolefins;

(2) from 10 to 50 wt% of a feed comprising C8-C10 aromatic compounds and having

(a) a level of aromaticity of from 13 to 45 wt% as determined by proton NMR,
(b) a softening point of from 50 to 100½C,
(c) an Mn of from 400 to 900 and an Mz of below 2200 and Mw below 1300 and a ratio of Mw/Mn of from 1.2 to 1.7

8. Use of the petroleum resin of claim 6 for tackification of styrene-butadiene block copolymer.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/01749

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 09 J 153/00, C 08 F 240/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 09 J; C 08 F

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	US, A, 4037016 (BRUCE W. HABECK ET AL) 19 July 1977, see column 1, line 46 - column 2, line 7; column 2, line 19 - line 24; column 2, line 54 - line 63; column 6, line 7 - line 11 --	1-8
Y	US, A, 4514554 (VINCENT L. HUGHES ET AL) 30 April 1985, see claim 1 --	1-8
Y	Dialog Information Services, File 350, World Patent Index 63-80, Dialog accession no. 76-94871x/51, NIPPON ZEON KK, "Adhesive compsn. contg. styrene butadiene block copolymer - with tackifier comprising hydrocarbon resin contg. 1,3-pentadiene and alpha-methyl styrene units", JP 51125134, A, 761101, 7651 (Basic) --	1-6

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
7th February 1991	05.03.91
International Searching Authority	**Signature of Authorized Officer**
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4704110 (GARY F. RAYKOVITZ ET AL) 3 November 1987, see column 7, line 1 - line 2	2
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 90/01749

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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For more details about this annex : see Official Journal of the European patent Office, No. 12/82